

Journals (*continued*).

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Coimbra 1884. The University.

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Hungarian Academy.

“Contributions to the Chemistry of Chlorophyll.” By EDWARD SCHUNCK, F.R.S. Received April 30, 1885. Read May 7, 1885.

Action of Acids on Chlorophyll.

Every one who has worked with chlorophyll must be familiar with the peculiar effect produced on the addition of acids to its solutions. If an alcoholic solution be taken, the colour of the solution changes when an acid is added from bright green to yellowish-green, and the spectrum at the same time undergoes alteration. After standing some time the solution gives a dark green deposit, which, after separation from the greenish-yellow liquid, shows when dissolved in boiling alcohol or ether, the spectrum of so-called “acid chlorophyll.”

This change is attributed by some to a simple modification of the chlorophyll; others consider it due to the formation of products of decomposition. The latter view is, I have no doubt, the correct one.

In order to obtain the products due to the action of acids on chlorophyll, I find it best to use hydrochloric acid. Fresh green leaves of any kind are extracted, without undergoing any preliminary treatment, with boiling spirits of wine. The extract, which should be of an intense green, is poured off from the exhausted leaves, and allowed to stand for a day or two. During this time, a light green somewhat slimy deposit is formed, consisting chiefly of wax and fatty matters coloured by chlorophyll.

On examining this deposit closely, it will almost invariably be found to contain, interspersed in the mass, small, red, glistening crystals. These crystals consist of a body first observed by Hartsen,* and called by him, “*chrysophyll*,” a name which it would be well to retain.† The deposit having been separated by filtration, a current of hydrochloric acid gas is passed into the dark green filtrate. This produces at once a dark green almost black voluminous precipitate,

* “Neue Untersuchungen über das Chlorophyll,” “Chem. Centralblatt,” 1875, S. 613.

† The erythrophyll of Bougarel and the crystallised xanthophyll of other chemists are doubtless identical with chrysophyll.

which increases in quantity on standing. After the precipitate has settled, the liquid appears greenish-yellow; it shows the spectrum of acid chlorophyll, due to the presence of colouring matters from the precipitate, these being not entirely insoluble in alcohol, but it also contains yellow colouring matters which darken the blue end of the spectrum, as well as other bodies extracted from the leaves which have no connexion with chlorophyll.

The dark green precipitate is now filtered off and washed with spirits until the filtrate appears nearly colourless. It contains besides impurities, which are chiefly of a fatty nature, two distinct colouring matters identical with the phyllocyanin and phylloxanthin of Fremy. These names I see no reason to change. They have been retained by Tschirch,* one of the latest writers on the subject. The method I adopt for separating the two substances is essentially the same as that of Fremy. I have tried other methods, but they have led to no result. The use of alkaline solvents is to be avoided, since both colouring matters are changed by the action of alkalis. The crude product of the action of the acid is first treated with ether, in which nearly the whole dissolves. The insoluble matter having been filtered off, the filtrate is mixed with about its own volume of fuming hydrochloric acid. The mixture, after being well shaken, is left to stand, when it separates into two layers, an upper yellowish-green one, containing phylloxanthin and a great part of the fatty matters, and a lower dark blue one, containing phyllocyanin. This is the experiment of Fremy, which is so often referred to in memoirs on chlorophyll, as having led him to the conclusion that chlorophyll was a compound or mixture of a blue and a yellow colouring matter. I propose first to give an account of phyllocyanin, the colouring matter of the blue layer.

The two liquids obtained in the manner just described are separated in the usual way, and the lower blue one is agitated with fresh ether, the process being repeated until the ether appears nearly colourless, and the phylloxanthin has been removed. After a short exposure, to allow the ether contained in it to evaporate, it is mixed with water, which produces a dark blue precipitate. This is filtered off, washed to remove hydrochloric acid, then dissolved in boiling glacial acetic acid. This solution on cooling gives a crystalline deposit of phyllocyanin, which is filtered off and recrystallised from acetic acid. If, on decomposing a little of it with boiling dilute nitric acid, nothing is left undissolved, the product may be considered pure, but if yellow oily drops appear on the surface of the boiling acid, the process of crystallisation from acetic acid must be repeated. The product is finally filtered off, washed with acetic acid, and dried.

By the process just described, I have obtained phyllocyanin from

* "*Untersuchungen über das Chlorophyll*," Berlin, 1884.

grass, from ivy leaves, from the leaves of the common thorn, and from the fronds of *Pteris aquilina*. No difference could be discerned between the different specimens obtained.

Properties of Phyllocyanin.

When dry, phyllocyanin has the appearance of a dark blue mass, which may easily be reduced to a fine powder. It resembles indigo, but when rubbed with a hard body it remains blue, and does not exhibit the coppery lustre which characterises indigo. Under a lens, small white glistening points are seen dotting the mass, produced by reflexion from crystalline surfaces. Examined under the microscope, it is found to consist almost entirely of elongated rhomboidal, or irregularly six-sided crystalline plates, which are generally opaque, but when very thin are translucent and then appear olive-coloured by transmitted light. Phyllocyanin is insoluble in water. It dissolves in boiling alcohol, but a great part of the substance dissolved separates out on the solution cooling, as a voluminous mass, consisting of microscopic crystals. It is more soluble in ether, glacial acetic acid, benzol, and carbon disulphide than in alcohol, but the best solvent is chloroform, which takes up large quantities of phyllocyanin even in the cold. A minute quantity of the substance imparts an intense colour to any of these solvents, especially chloroform. It is only on diluting largely that these solutions lose their opacity. They then appear of a dull green or olive colour, and show the well-known and often described spectrum of "acid chlorophyll," consisting of five bands of various intensity. The solutions fluoresce, but not so strongly as solutions of chlorophyll.

When the ethereal solution is mixed with concentrated hydrochloric acid, the whole of the phyllocyanin is taken up by the acid, yielding a dark greenish-blue solution, which sinks to the bottom. Should phylloxanthin be present, it will be found in the upper ethereal layer, which then shows a yellowish-green tint, and an absorption spectrum differing from that of phyllocyanin. The lower greenish-blue solution shows when sufficiently dilute five absorption bands, the spectrum, in fact, of the hydrochloric acid compound of phyllocyanin, which differs widely from that of phyllocyanin itself.

Phyllocyanin is almost insoluble in boiling petroleum ether, and nearly insoluble in ligroin. It dissolves easily in warm aniline.

Phyllocyanin contains nitrogen, but is free from sulphur.

Action of Heat.—When heated on platinum, phyllocyanin gives off an acid smell, then swells up considerably, evolving gas which burns with a smoky flame, and leaves a voluminous charcoal, which burns away slowly, a hardly visible trace of ash being left. When heated slowly between two watch-glasses, it swells up slightly, and

becomes charred. On the lower glass there is left a black mass which imparts no colour to boiling chloroform, and seems to be simply charcoal. On the upper glass, there is found a small quantity of brownish sublimate, which, under the microscope, is seen to consist partly of crystalline needles, partly of regular rhombic crystals which are honey-yellow by transmitted light.

When slowly heated in an air bath to 160° , phyllocyanin remains apparently unchanged. It is still completely soluble in chloroform, the solution showing the usual absorption bands. On heating, however, to 180° , complete decomposition takes place, but without any change of volume in the substance. The charred mass now imparts to boiling chloroform only a very faint green tinge, and when heated in a tube, gives off no empyreumatic products, only a slight odour of hydrocyanic acid.

Action of Oxidisers.—On adding a little nitric acid to a boiling saturated solution of phyllocyanin in glacial acetic acid, the solution immediately becomes yellow, but without evolution of nitrous fumes. It deposits nothing on cooling and standing. On the addition of water it gives a dirty green flocculent precipitate, the filtrate from which is still yellow, but shows no absorption bands. The precipitate dissolves easily in alcohol, giving a yellow solution, which shows a spectrum differing from that of phyllocyanin.

Phyllocyanin itself, treated with boiling dilute nitric acid is rapidly decomposed and dissolved with evolution of nitrous fumes. The solution evaporated in the water-bath leaves a residue which, treated with water, dissolves in part. The filtrate has a bitter taste, and leaves, on evaporation, a soft yellow residue, in which, on standing, some colourless crystalline needles are formed. The portion insoluble in water dissolves easily in alcohol, giving a yellow solution which, on evaporation, leaves a residue having a crystalline appearance, but not really crystalline when examined under the microscope.

A hot concentrated solution of phyllocyanin in glacial acetic acid becomes, on the addition of a little chromic acid, yellowish-green, but deposits nothing on cooling. The solution gives with water a dull green precipitate, the filtrate from which is yellow, and shows no absorption bands, while the precipitate itself, treated with ether, gives a solution which differs somewhat as regards colour and absorption bands from a solution of phyllocyanin.

Phyllocyanin treated with a watery solution of chromic acid, to which a little sulphuric acid has been added, is decomposed with much effervescence, giving a green solution, which, after evaporation, leaves a residue yielding to solvents only amorphous products.

Insolation.—I will introduce here what I have to say regarding the effect of insolation on phyllocyanin, because there can be no doubt

that the effects observed are due to oxidation. Anyone who has observed the ease and rapidity with which a solution of chlorophyll is bleached on exposure to light and air would be struck with the extraordinary permanence exhibited by phyllocyanin under the same circumstances. A moderately strong solution of phyllocyanin when exposed to sunlight retains its colour for a long time, the last trace disappearing only after many weeks' exposure.

In order to observe the changes which take place, it is best to take a chloroformic solution of phyllocyanin and expose it to sunlight in a loosely-stoppered bottle, the stopper being occasionally removed, and the contents shaken. The green colour of the solution gradually becomes fainter, the absorption bands of phyllocyanin remaining visible. After some time the colour changes to yellow, but the solution still shows a strong band in the red, corresponding to band I of phyllocyanin. At length this band also disappears, and there is now nothing to be seen but the total obscuration at the blue end of the spectrum, which most yellow solutions show. In one experiment the chloroformic solution was exposed to alternate bright sunlight and diffused daylight from the middle of April to the middle of June, when it was filtered from a flocculent yellow deposit which had formed. A further exposure to the middle of August was required to cause the entire disappearance of the band in the red.

Several products are formed during this process of insolation. The first consists of a flocculent yellow deposit, which gradually separates from the chloroformic solution. This deposit, after filtering off and washing with chloroform, is found to be easily soluble in alcohol and caustic alkali, but insoluble in boiling water, in which it simply melts; insoluble also in ether, ligroin, and carbon disulphide. The alcoholic solution is yellow, shows no absorption bands, and leaves, on spontaneous evaporation, a residue which has a somewhat crystalline appearance, but is found to be amorphous when examined under the microscope. The chloroformic filtrate leaves, on evaporation, a residue, which, on treatment with hot water, dissolves only in part. The part left undissolved by water resembles the product deposited from the chloroformic solution. It melts in boiling water; it is easily soluble in alcohol, the solution being yellow and leaving, on evaporation, a pale yellow brittle amorphous residue; it is insoluble in ether and carbon disulphide. The watery filtrate from this second product, after treatment with animal charcoal, which deprives it of most of its colour, leaves, on evaporation over sulphuric acid, a pale yellow transparent gum-like residue, in which nothing crystalline can be detected, and of which the following are the most characteristic reactions:—

Heated on platinum it is decomposed, giving off acid fumes with an odour like those from heated tartaric acid, leaving much charcoal;

its watery solution has a strong acid reaction and a sour and at the same time very bitter taste; the solution gives no coloration with ferric chloride; it evolves ammonia when boiled with caustic potash, and it reduces Fehling's solution on boiling.

It appears, therefore, that by insolation, phyllocyanin yields products which resemble, if they are not identical with, those due to the action of nitric and chromic acids. It is possible that some of these products may be contained in faded autumnal leaves after the chlorophyll has disappeared, but their indefinite character would render their identification very difficult. Green leaves, in becoming yellow, pass through a stage in which they yield when treated with alcohol an extract which, though quite yellow and non-fluorescent, shows a strong absorption band in the red. Of this fact I was forcibly reminded when watching the progressive changes of phyllocyanin during insolation.

Action of Chlorine.—On passing a current of chlorine gas through a chloroformic solution of phyllocyanin, the first effect observed is a change of colour in the solution from dull green to a bright grass-green, the latter colour closely resembling that of a solution of chlorophyll. The solution shows an absorption spectrum which coincides neither with that of chlorophyll nor with that of phyllocyanin.

On standing for a day or two the solution loses its bright green colour, and acquires a reddish hue, with a green tint at the edges where the thickness of the liquid is less. It now shows the same number of bands as a phyllocyanin solution, but the bands are all nearer the red end. On evaporation it leaves a greenish-brown amorphous residue. On passing more chlorine through the chloroformic solution of phyllocyanin the green colour seen at first disappears, the solution becomes yellow, at last pale yellow, all the bands characteristic of phyllocyanin at the same time disappearing. The liquid leaves, on evaporation, a yellow amorphous residue like resin. This, after heating in the water-bath to drive away all traces of hydrochloric acid, is found to contain chlorine. It does not dissolve in boiling water, but merely softens. It is easily soluble in alcohol, the solution being yellow and showing much obscuration in the blue of the spectrum, but no absorption bands even when very dilute. It dissolves only in part when treated with caustic potash lye.

Action of Bromine.—On the addition of a little bromine to a chloroformic solution of phyllocyanin, the solution acquires a bright grass-green colour, and now shows four absorption bands. On adding an excess of bromine to the solution, heating and evaporating, an olive-coloured amorphous product, containing bromine, is obtained, which dissolves easily in alcohol. The solution is brownish-red, and shows a spectrum similar to that of phyllocyanin, but having the bands all nearer the red end.

Action of Acids.—A mixture of 1 part of concentrated hydrochloric acid with 9 parts of absolute alcohol, dissolves phyllocyanin easily. In daylight the solution appears dark blue, green at the edges; in artificial light it appears purple. It shows a spectrum differing from that of phyllocyanin, and more nearly resembling that of chlorophyll, especially as regards the fourth and fifth bands, which are extremely faint, whereas with phyllocyanin they are very intense; the spectrum is, in fact, that of the hydrochloric acid compound of phyllocyanin. On adding water to the solution, unchanged phyllocyanin is precipitated, but if the solution be evaporated, it leaves a residue green by transmitted, blue by reflected light, which is no longer phyllocyanin, for it dissolves in alcohol with a brownish-green colour, and the solution shows a spectrum identical with that of the product formed by the action of alkalis on phyllocyanin, and characterised by two bands in the red, and two fine, but distinct bands in the green, which will be referred to presently.

Phyllocyanin is soluble in concentrated hydrobromic acid.

It dissolves in concentrated sulphuric acid, giving a grass-green solution, which shows a spectrum resembling that of the hydrochloric acid compound. On the addition of water, unchanged phyllocyanin is precipitated, but if the solution be left to stand for some time, the phyllocyanin contained in it is changed, and the precipitate with water now consists of several products, one of which shows the same spectrum as that formed by the action of hydrochloric acid.

Phyllocyanin is not in any way affected by treatment with a boiling watery solution of phosphoric acid. On the addition of phosphoric acid to a boiling alcoholic solution of phyllocyanin, the latter acquires a purplish tint, but the spectrum remains the same, and the solution on cooling deposits unchanged phyllocyanin.

Phyllocyanin shows no tendency to combine with oxalic, tartaric, or citric acid, but these acids do affect it to a certain degree, that is, they induce decomposition at temperatures at which the substance itself remains unchanged. Mixtures of finely powdered phyllocyanin with oxalic, tartaric, and citric acids remain unaltered when heated in the water-bath. After being heated in an air-bath to 130°, the oxalic acid mixture no longer contains phyllocyanin, the latter being completely charred and decomposed, whereas the tartaric and citric acid mixtures show only slight indications of change at that temperature. On being heated to 155°, and kept at that temperature for some time, the tartaric and citric acid mixtures are found to contain products which differ from phyllocyanin, without having properties such as compounds of the latter with acids might be expected to show. Under the conditions described, therefore, phyllocyanin shows no tendency to combine with weak acids.

Action of Alkalis.—When phyllocyanin is treated with very dilute

caustic potash or soda-lye, it dissolves entirely. The solution has the same colour as other phyllocyanin solutions, and shows a similar spectrum, but with the bands less distinctly marked. It gives precipitates of various shades of green, with earthy and metallic salts, such as the chlorides of barium and calcium, lead acetate, and copper acetate. These might, perhaps, be regarded as compounds of phyllocyanin, and be called phyllocyanates. Nevertheless it is easy to show that by mere solution in alkali, phyllocyanin undergoes a complete change. If the alkaline solution be mixed with an excess of acetic acid, and then shaken up with ether, the precipitate with acid dissolves in the ether, the solution having the colour of a phyllocyanin solution, and showing the characteristic absorption-bands; but if the solution be left to stand in contact with excess of acid for some time, its colour changes from olive to a brown or smoke colour, and it now shows quite a different and very elegant spectrum, characterised by two bands in the red, one of which is thin and nearer the red end than the first band of phyllocyanin, and two very fine but distinct bands in the green, the third and fourth bands of phyllocyanin having disappeared, while the fifth still remains. Since phyllocyanin, before solution in alkali, is not changed appreciably by acetic acid, even on boiling, it is evident that by the action of alkali it is in some way metamorphosed, so as to be liable to further change when acted on by the acid. In preparing this product of the successive action of alkali and acid, care must be taken to operate in the cold, for if hot alkaline lye be used, an entirely different product is formed. It is deposited from a boiling alcoholic solution in microscopic crystals, which are quite opaque, even in a strong light, and resemble crystallised phyllocyanin. In none of the various memoirs on chlorophyll that have come under my notice have I seen any spectrum figured or described at all resembling that of the solutions of this substance. The spectrum is distinctly seen, even in exceedingly dilute solutions.

The next product of the action of alkalis on phyllocyanin is formed when hot alkaline lye is employed. In order to obtain it, a solution of phyllocyanin in boiling alcohol is mixed with alcoholic potash or soda, and boiled. On standing, the solution yields a semi-crystalline deposit of a fine purple colour by reflected light, consisting of a potassium or sodium compound of the product formed. This is filtered off, washed with alcohol, and then dissolved in water. The solution gives with acetic acid a green flocculent precipitate, which is filtered off, washed, and dissolved in boiling glacial acetic acid. This solution on standing deposits small crystalline rosettes, which are green by transmitted light, and of a fine purple by reflected light. The solutions of this substance have a dull purple colour, and exhibit a distinct spectrum, characterised by a broad very dark band in the green.

I shall return to these products on a future occasion.

Phyllocyanin does not dissolve very readily in ammonia.

Action of Aniline.—When a solution of phyllocyanin in aniline is slowly evaporated, a residue is left consisting partly of dark granules of phyllocyanin, partly of pale purplish-brown crystalline needles, arranged in tufts and rosettes. The latter may be either a compound with aniline, or a product of the action of aniline on phyllocyanin at the ordinary temperature; it is formed in minute quantities only. A more energetic action takes place at higher temperatures. When aniline and phyllocyanin are heated together in a sealed tube to 130° and kept at that temperature for some time, a complete change takes place. The contents of the tube on being poured into alcohol dissolve in part only, a crystalline mass being left undissolved, the filtrate from which is greenish-brown, and shows the peculiar spectrum of the first product of the action of alkalis on phyllocyanin. The crystalline mass on the filter dissolves partly on treatment with boiling alcohol, and the filtered liquid deposits on cooling a quantity of white crystalline needles in star-shaped groups, which are soluble in ether and chloroform, but insoluble in dilute acids and alkaline lyes. The portion of the crystalline mass left undissolved by boiling alcohol dissolves in chloroform. The solution is red, and shows a very characteristic spectrum, consisting of three fine but very distinct bands in the red, of which the central one is the strongest, one very dark band covering the yellow and part of the green, which, when the solution is so far diluted as to show only two bands in the red, splits up into two nearly equal bands, and lastly, one dark band at the edge of the green and blue. The chloroformic solution leaves, on evaporation, a semi-crystalline residue, having a purplish hue.

It might be supposed that on treatment with ammonia, phyllocyanin would yield products similar to those formed by the action of aniline, but this is not the case. When phyllocyanin is heated with strong liquor ammoniæ in a sealed tube to 140° , bodies are formed which are similar to if not identical with those due to the action of fixed alkalis.

Compounds of Phyllocyanin.—From what has been stated above, it may be inferred that phyllocyanin plays the part of a weak base, that is, it combines with strong acids, the compounds however being unstable, and easily decomposed even by water. Like other weak bases, it may also act as an acid, though for reasons before mentioned, it may be doubted whether, in combining with bases, it does so without undergoing change. Notwithstanding its nearly neutral character, however, phyllocyanin is capable of yielding compounds of great comparative stability, into which metals and acids, especially organic acids, enter as constituents.

When phyllocyanin is dissolved in boiling glacial acetic acid, it

crystallises out unchanged on the solution cooling. The same happens when freshly precipitated cupric oxide or zinc oxide is added to a boiling alcoholic solution of phyllocyanin; the solution deposits phyllocyanin, and there are no indications of any combination taking place between the phyllocyanin and the metallic oxide.

A very different effect is observed when either of the two oxides is employed along with acetic acid. When cupric oxide is added to a solution of phyllocyanin in boiling acetic acid, the solution acquires at once a deep greenish-blue colour, and it no longer contains uncombined phyllocyanin, for its spectrum is different, and on standing it deposits lustrous crystals, which doubtless consist of a compound of which phyllocyanin, acetic acid, and copper are essential constituents. If zinc oxide be employed, a similar effect is observed; the liquid acquires an intense green colour, and now contains the corresponding acetate of phyllocyanin and zinc.

The same phenomenon is seen when ferrous oxide, manganese oxide, or silver oxide, or one of the corresponding acetates is taken, solutions of various shades of green being obtained, which contain phyllocyanin compounds, but no similar compounds are formed when potassium, sodium, barium, calcium, magnesium, or lead acetates are employed, for on adding the acetate of any of the last-named metals to an acetic acid solution of phyllocyanin, the colour of the latter remains unchanged, and phyllocyanin is deposited, just as if no metallic acetate were present. Acetic acid is, however, not the only acid which yields the reaction. If palmitic, stearic, oleic, tartaric, citric, malic, or phosphoric acid be employed, it takes place just as with acetic acid, but, in some cases, time is required for its completion. The process results, there can be little doubt, in the formation of compounds analogous to those with acetic acid. To obtain these compounds, it is only necessary to add a little of the freshly precipitated metallic oxide, and an excess of one of the acids named, to a solution of phyllocyanin in boiling alcohol, keeping the solution boiling for several hours, then filtering and adding water, in which the compounds are insoluble. The precipitated compounds, which are generally of a bright green, are filtered off and washed before treatment with reagents.

The following is an enumeration of the compounds obtained in the way just described:—

Phyllocyanin cupric acetate.

„	„	palmitate.
„	„	stearate.
„	„	oleate.
„	„	tartrate.
„	„	citrate.
„	„	phosphate.

Phyllocyanin argentic acetate.

„ zinc acetate.
 „ „ palmitate.
 „ „ stearate.
 „ „ oleate.
 „ „ citrate.
 „ ferrous acetate.
 „ „ palmitate.
 „ „ oleate.
 „ „ citrate.
 „ „ malate.
 „ „ phosphate.
 „ manganese acetate.

It would, of course, be easy to extend this list by taking a greater variety of acids and metallic oxides.

Nevertheless, strange to say, several compounds, the existence of which might have been anticipated, are not formed under the same conditions as those above enumerated. Phyllocyanin does not enter into combination when its alcoholic solution is boiled with cupric oxide and oxalic acid, zinc oxide and oxalic acid, zinc oxide and tartaric acid, ferrous oxide and tartaric acid. I could also see no indication of double compounds of phyllocyanin hydrochloride with the chlorides of platinum, mercury, or copper being formed, but on the other hand, a double sulphate of phyllocyanin and copper seems to exist. Attempts to form compounds by heating mixtures of phyllocyanin with glycerin and various fatty acids, at a temperature of 130°, led to negative results.

The various compounds above enumerated have a number of properties in common, though the several classes differ, *inter se*, in some important particulars.

They all dissolve more or less easily in alcohol, ether, chloroform, benzol and carbon disulphide, in fact in all the solvents which take up phyllocyanin and chlorophyll, but they are all insoluble in water, with the exception of the phyllocyanin manganese acetate, which dissolves readily therein. The solutions have a green colour, varying from grass-green, like that of chlorophyll solutions, to a fine bluish-green or blue, and they show peculiar spectra. The alcoholic solutions remain quite unchanged when sulphuretted hydrogen is passed through them, no precipitate is formed, and the solutions, on evaporation, leave the various compounds with their original properties unchanged. It is only on incineration that the presence of the metallic constituents is detected, the copper compounds leaving, after being burnt, cupric oxide; the zinc compounds, zinc oxide, the iron compounds, ferric oxide. Lastly, they are all soluble in dilute alkaline lyes, and are again precipitated unchanged on the addition of acetic

acid. These reactions make it somewhat doubtful whether these compounds are to be considered as double salts in the ordinary acceptation, and whether the metallic constituents may not rather be contained in them somewhat in the same way as the iron in hæmatin.

I have still a few remarks to make on the distinctive properties characterising the three principal groups of these compounds, the cupric, zinc, and ferrous groups.

Of these, the cupric compounds are the most beautiful, and, at the same time, the most stable. Their solutions show a brilliant colour, inclining more to blue than green, and spectra with four absorption bands, the position of which varies somewhat according to the acid employed. They are not decomposed by treatment with strong acids. If an alcoholic solution of any one of them be mixed with a large quantity of hydrochloric acid and boiled, the colour is not changed, and on adding water, and then shaking up with ether, the ethereal liquid which rises to the surface shows the same colour and the same spectrum as the original alcoholic solution. The phyllocyanin cupric acetate is the most beautiful of the series. It is best prepared by adding cupric acetate to a solution of phyllocyanin in boiling acetic acid. The crystalline mass which separates out on standing is filtered off, treated with dilute hydrochloric acid to remove any excess of cupric acetate that may be present, and then redissolved in glacial acetic acid boiling. The solution on cooling deposits the compound in crystalline scales, which are elongated, pointed at the ends, of a pale greenish-blue by transmitted light, and of a brilliant purple, with a semi-metallic lustre, by reflected light; it much resembles crystallised indigo-blue. The other cupric compounds yield only microscopic crystals.

The zincic group of compounds yield solutions of a brilliant green, showing spectra of five bands. These compounds are distinguished from the preceding by their instability in the presence of strong acids. If an alcoholic solution of any one of the zinc compounds be mixed with hydrochloric acid and boiled, its colour changes to blue. On now adding water, the blue colour disappears, and a precipitate is formed which on shaking up with ether dissolves. The ethereal solution has the colour and shows the absorption spectrum of phyllocyanin solutions. The zinc compounds are therefore decomposed by hydrochloric acid, yielding phyllocyanin again as one of the products of decomposition.

The behaviour of phyllocyanin towards zinc oxide in the presence of organic acids may serve to explain a peculiar phenomenon first observed by Church* and subsequently described by Tschirch. The former took chlorophyll that had become olive-brown on standing, and, acting on it with zinc powder in the water-oven, obtained a body

* "Chemical News," xxxviii, 168.

yielding bright green solutions, which he took to be regenerated chlorophyll. Tschirch acted on Hoppe-Seyler's chlorophyllan with zinc powder, and observed the same phenomenon, the conclusion at which he arrived being the same, viz., that chlorophyll is reproduced from chlorophyllan by the reducing action of zinc. I think, however, that what Tschirch obtained was, in reality, a zinc compound, and would have been formed just as well by using zinc oxide. Chlorophyllan is probably an impure substance, containing, it may be, some fatty acid, together with phyllocyanin, so that by the action of zinc oxide on the mixture a compound similar to those above described may be formed.

I have tried the experiment with the precipitate produced by treating a chlorophyll solution with hydrochloric acid, which probably differs very little from chlorophyllan, dissolving it in boiling alcohol, adding zinc oxide and boiling for some time, when a bright green liquid was obtained, which might have been taken for a solution of chlorophyll, but evidently contained a zinc compound of the same character as those formed directly from phyllocyanin by a similar process. The spectrum was identical with that of the zinc compounds from phyllocyanin.

The ferrous group of compounds yield solutions of a pure green, like that of chlorophyll. They are not, however, strikingly fluorescent, and when exposed to sunlight in open vessels they retain their colour unchanged for a long time. The group may be divided into two sub-groups: the first sub-group comprising compounds into which one of the fatty acids—acetic, palmitic, or oleic acid—enters as a constituent; the other sub-group, such as are formed by the action of citric, malic, or phosphoric acid. The members of the first sub-group show, in solution, the same spectrum, consisting of four ill-defined absorption bands, with much obscuration throughout. To the other group belongs a spectrum consisting also of four bands, which are, however, differently placed and more distinct than with the first sub-group. If a small quantity of hydrochloric acid be added to an alcoholic solution of any one of the iron compounds the solution acquires a blue tint, and the bands are now found to have shifted considerably towards the blue end. This effect may be due to the removal of a portion of the iron, and the formation of compounds with less iron. If a member of the second sub-group be taken, the phosphate or the malate for instance, then on the addition of hydrochloric acid a spectrum is obtained which closely resembles the ordinary chlorophyll spectrum as regards the number, position, and relative strength of the bands. The members of the first sub-group undergo a further change by treatment with an excess of hydrochloric acid and boiling, but the resulting product is not phyllocyanin.

All the members of the iron group of compounds undergo a peculiar change by the action of ether. When the alcoholic solution of any one of them is mixed with its own volume of ether, the green colour gradually fades and gives place to yellow. All the bands except that in the red disappear, while another fine band further in the red makes its appearance. At length the two bands in the red also vanish, and nothing is now seen but a considerable obscuration at the blue end, due to the presence of a yellow colouring matter in solution. The change resembles that which is seen on exposure of a chlorophyll solution to air and sunlight; it takes place, however, quite as readily in a closely stoppered bottle, kept in the dark, as in an open tube exposed to light. It is effected more rapidly by ordinary methylated ether than by pure ether. Benzol and acetone act in the same way as ether, but chloroform and carbon disulphide are without effect.

The phyllocyanin manganese acetate, which is obtained by adding manganese acetate to a solution of phyllocyanin in glacial acetic acid, differs from the compounds previously described by its solubility in water. It also dissolves easily in alcohol, but less readily in ether and benzol. Its solutions are green, like those of the iron compounds, and show a peculiar spectrum. It is not changed by treatment with boiling hydrochloric acid, and its alcoholic solution remains unaltered when mixed with ether or benzol.